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Electrofreezing of water in molecular dynamics simulation accelerated by oscillatory shear

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We present a study of the effect of oscillatory shear on the crystallization of supercooled water in nonequilibrium molecular dynamics simulations of simple water models. [The TIP4P model has been used throughout; calculations using the extended simple point charge (SPC/E) model were checked for consistency and gave qualitatively the same results.] The application of a planar Couette flow field alone did not result in crystallization but in combination with a static electric field different isomorphs of ice emerged depending on the state of the system. At high pressures $(3-5\ \mathrm{kbar})$ the oscillatory shear substantially speeded up the formation of the conjectured ice polymorph (ice XII). At ambient pressures lower density systems could be forced to order in situations where hitherto the application of the electric field alone has not resulted in ordering. These results suggest that this method will be very useful in exploration of the fluid-solid boundaries of the phase diagram of models for water. [S1063-651X(97)51212-8]

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Water is of abiding scientific interest since it is nature's most important solvent in biological and chemical processes, yet the origins of its remarkable properties are far from understood. The availability of powerful computers and simple but accurate models for water make it increasingly feasible to perform molecular simulation of liquid water over timescales that are large relative to its intrinsic translational and rotational relaxation times. Such long simulations are necessary if one wishes to study complex many-body phenomena in water, such as phase transitions.

Because of their application to biological systems and to chemistry at ambient conditions, essentially all intermolecular potential models for water [such as the TIP4P [1] and the extended simple point charge (SPC/E) [2] models, which were used in the study reported in this paper] have been developed by fitting to experimental data at or around room temperatures. The models are thus very successful in reproducing many water properties at ambient conditions but have only recently been applied at significantly lower [3–6] or higher [7,8] temperatures. The first direct simulation of the freezing of a bulk sample of water (or, for that matter, *any* molecular fluids) was reported recently by Svishchev and Kusalik [4,5]. These authors demonstrated that the application of a static electric field to supercooled TIP4P water samples transformed the water to crystals. Because of the applied field, highly polarized cubic ice I (I_c) was formed instead of the most common hexagonal ice I (I_h). Shortly thereafter, the same authors found a previously unknown polymorph of ice (which they denoted ice XII) using the same electrofreezing process (i.e., applying a static homogeneous electric field to a supercooled liquid). In this case, the supercooled TIP4P water samples were in the temperature range $225-240$ K and under pressures of $3-5$ kbar in molecular dynamics simulations [6]. This open quartzlike structure was formed after about 1 ns, which can be regarded as quite a slow transformation when compared to the formation of cubic ice I at lower pressure but higher temperature in about 200 picoseconds (ps) [4,5]. The applied electric field ~ 0.5 V/Å is very strong, but is comparable to that experienced by water molecules within molecular distances of the surfaces of biopolymers [9] and within the cracks of amino acid crystals [10].

The crucial step in the formation of these crystals is the complete breakup of liquid water's hydrogen bonding network. In the electrofreezing process simulated by Svishchev and Kusalik, the sample will be completely polarized when the original hydrogen-bonded network is distorted and/or broken up sufficiently for the molecules to align with the applied field. We began the work reported herein by hypothesizing that another form of external field may be able to break up the hydrogen-bonded network. The action of the field should result in perturbation of the molecular positions and possible reorientation of the hydrogen bonds to facilitate the molecules exploring phase space and locating the minimum energy configuration associated with the solid state. Experimentally, for example, it is known [11] that the application of ultrasound on supercooled water samples can speed up the phase transition. In partial analogy to this, the simplest physically realizable external field to impose in a molecular dynamics simulation is an oscillatory planar Couette flow with shear rates $\dot{\gamma}_{\alpha\beta}=\partial v_{\alpha}/\partial\beta$ $(\alpha,\beta\in\{x,y,z\}$ and $\alpha\neq\beta)$ varying from $-\dot{\gamma}_{\alpha\beta,0}$ to $\dot{\gamma}_{\alpha\beta,0}$ given by

$$\dot{\gamma}_{\alpha\beta}=\dot{\gamma}_{\alpha\beta,0}\cos(\omega t). \tag{1}$$

However, we found that oscillatory shear alone could not induce crystallization from supercooled TIP4P water samples. We concluded that this is due to the inability of oscillatory shear to significantly affect the orientation of individual molecules, an important factor in the difference between freezing phenomena in atomic and molecular liquids. In the following we describe the combined effect of an oscillatory shear in combination with a static electric field on supercooled TIP4P water in molecular dynamics simulations.

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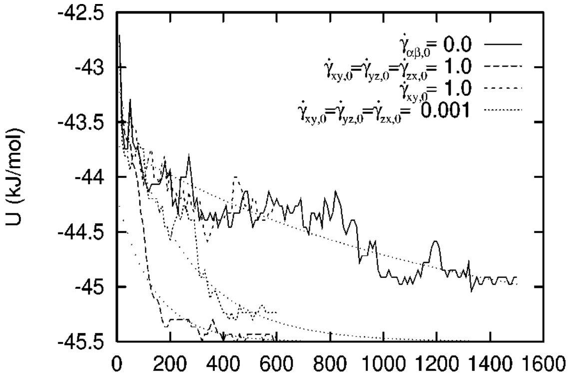

FIG. 1. The configurational energy (in kJ/mol) plotted against time (in ps) for the electrofreezing process. The smooth dotted lines are the exponential fits described in the text. The full, long-dashed, small-dashed, and broken lines represent data from runs with $\dot{\gamma}_{\alpha\beta,0}=0.0$, $\dot{\gamma}_{\alpha\beta,0}=1.0$, $\dot{\gamma}_{xy,0}=1.0$, and $\dot{\gamma}_{\alpha\beta,0}=0.001$, respectively.

Together, oscillatory shear and electrofreezing proved to be much more effective than electrofreezing alone.

In our simulations we used 256 particles in a cubic cell with the usual periodic boundary conditions. To impose shear, the Sllod algorithm [12] (so named because of its close relationship to the Dolls tensor algorithm) has been used along with the Lees-Edwards periodic boundary conditions. The TIP4P rigid water model has been used for the interactions (for a description of the model, see in Ref. [1]). Calculations with the SPC/E water model yielded qualitatively the same results and will be discussed in detail elsewhere [13]. The long range electrostatic interactions were handled by using the reaction field method [14]. The equations of motion were integrated by a fourth-order Gear predictor-corrector method with a timestep of 0.001 ps. The motion of the molecular sites was implemented using the Evans-Murad quaternion algorithm [15] and the temperature kept constant by using a Gaussian thermostat [12]. The constant electric field was applied in the z axis direction in the laboratory frame.

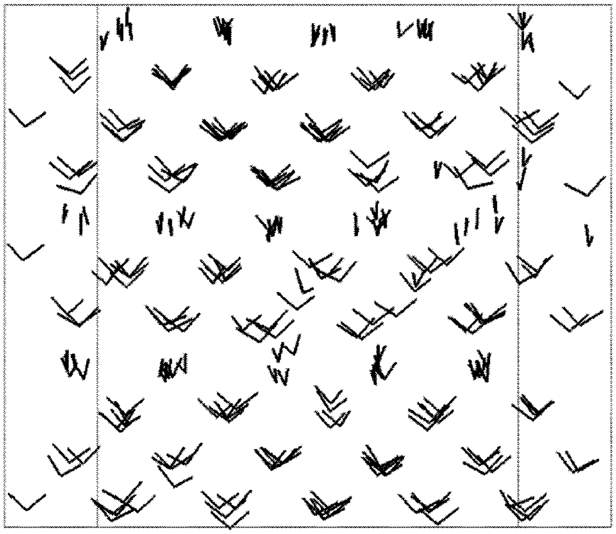

FIG. 2. Snapshot of the molecules in the x-z plane after 200 ps of combined shearing and electrofreezing followed by electrofreezing alone for 200 ps, with an applied maximum shear rate of unity and electric field 0.5 V/Å. The direction of the homogeneous electric field (laboratory z axis) is vertical in the plot. ($\rho=1.17$ g/cm^3, $T=230$ K.)

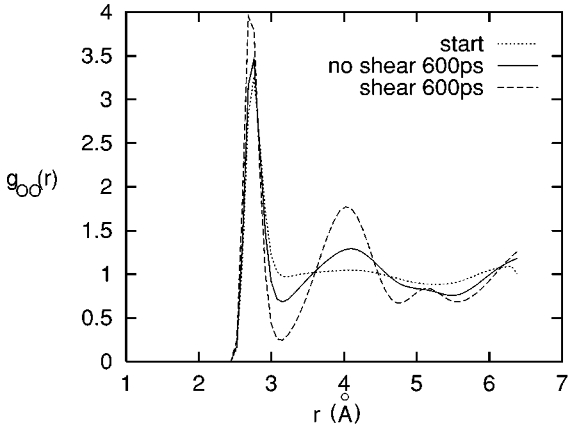

FIG. 3. The oxygen-oxygen pair correlation function $g_{OO}(r)$ as a function of the O-O distance r (in Å) for several samples. The $g_{OO}(r)$ of the sample just before turning on the electric field (dotted line) is shown along with that of the sample after 600 ps of electrofreezing with (dashed line) or without (full line) applying oscillatory shear. ($\rho=1.17$ g/cm^3, $T=230$ K.)

We begin by considering the formation of the new high density crystal, ice XII [6]. In our constant volume simulations we set the density to 1.17 g/cm^3. The preparation of the supercooled samples was as follows: We began with a liquid configuration that was equilibrated for 300 ps at 298 K, then cooled to 230 K and equilibrated for another 300 ps.

In Fig. 1 we plotted the configurational energy vs time of four different simulation runs. The longest curve is for the electrofreezing without any applied shear. After about 1000 ps the ice XII crystal forms. (The unit cell is described in Ref. [6]; a snapshot of the simulation box is shown in Fig. 2.) It contains defects, so turning the field off would result in melting of the crystal. Defects can be eliminated (and the crystal conserved) by cooling down even further [4]. Two other curves attain a lower energy (meaning less defects in the crystal) in substantially less time; we will return to these curves shortly. First, however, we consider the fourth curve (small dashed line in the figure) which is barely visible, since it closely follows the first curve but terminates at an earlier time. In this run, the oscillatory shear is $\dot{\gamma}_{xy,0}=1.0$ in reduced units (corresponding to 6×10^{11} Hz in real units) and it is applied without interruption for the first 200 ps of the run, and always in the x direction of the laboratory coordinates. After 200 ps, shearing was turned off, with the electric field remaining on. The reason for this is that once the crystal is formed, it can be broken up by the constant motion due to the applied shear. Thus the application of shear should be thought of as providing a ‘‘kick’’ for the system to converge to the energetically favorable crystal state, and hence should be applied for a limited time. However, the figure clearly shows that this method does not improve the crystal formation. In subsequent simulations, we applied a more elaborate method in that we permitted the system to relax for a period after each shearing period, and applied the shear in the y and z directions as well. Specifically, the simulation proceeded as follows: The electric field was turned on (in the z axis direc-

TABLE I. Parameters of the exponential fit [$y=-45.5+A\exp(-t/\tau)$] to the configurational energy (in kJ/mol) vs time (in ps) curves in Fig. 1 along with the regression constant, R. The characteristic time (in ps) for the formation of the crystal is τ, while $\dot{\gamma}_{\alpha\beta,0}$ refers to the maximum shear rate (in reduced units) used in the particular simulation.

$\dot{\gamma}_{\alpha\beta,0}$	A	τ	R
0.0	1.790	1222	0.890
0.001	2.370	233	0.948
1.0	1.327	136	0.955

tion) and remained on throughout the simulation. The oscillatory shear was turned on for only 1 ps [corresponding to one period of oscillation of the shear, since ω in Eq. (1) was set to 2π ps^{-1}] in the x direction, then turned off for 3 ps for the system to relax, followed by another 1 ps of shearing in the y direction followed by a 3 ps relaxation, then 1 ps of shearing in the z direction followed by a 3 ps relaxation. This process was repeated throughout the first 200 ps of the simulation. After 200 ps, shear was no longer applied to the system. Results for $\dot{\gamma}_{\alpha\beta,0}=1.0$ and 0.001 are included in Fig. 1.

Clearly, the application of oscillatory shear significantly enhances the relaxation towards the crystalline state. To quantify this enhancement, the configurational energy (in kJ/mol) vs time (in ps) curves were fitted to the equation $y=-45.5+A\exp(-t/\tau)$ and the fits are shown with smooth dotted curves in Fig. 1. The parameters A and τ along with the regression constant R are listed in Table I. It is clear that the time needed for the crystallization is reduced by an order of magnitude through the use of oscillatory shear combined with the electric field. It should also be noted that the gain in speed is still fivefold with the application of a shear rate of 10^{-3} in reduced units, which in the realm of nonequilibrium molecular dynamics simulations is very small (i.e., inducing a response comparable to the thermal noise level in the simulation) [12].

A snapshot of the resulting configuration can be seen in Fig. 2. For clarity, only the O–H bonds are drawn. Note that the crystal is fully proton-ordered. The polarization rate, defined as the average of the dot products of the bond bisectors with the field, is roughly 97%. First, it should be noted that the cubic simulation cell is not commensurate with the conjectured ice XII lattice in Ref. [6]. This means that a perfect lattice cannot be expected in our simulations. The characteristic features of the ice XII lattice can be identified in the picture. However, the unit cell itself cannot be found, since a structure very similar to ice XII commensurate with the cubic cell has emerged. For this reason, conventional application of the translational order parameter of the ice XII lattice [6] does not serve as an indicator of the phase transition. The quantities that best indicate the ordering are the configurational energy (see Fig. 1), the instantaneous hydrostatic pressure and the oxygen-oxygen pair correlation function $g_{OO}(r)$. This signature of crystalline packing, alternating hexagons and rhombuses in the projections parallel with the electric field, can also be identified in a simulation of water between charged Pt surfaces [16]. The structure is slightly different there as well, which can be regarded as a consequence of small simulation cells. In Fig. 3 we plotted the $g_{OO}(r)$ of our sample at the beginning, in the middle, and at the end of the electrofreezing process. The last curve shows almost perfect crystalline order.

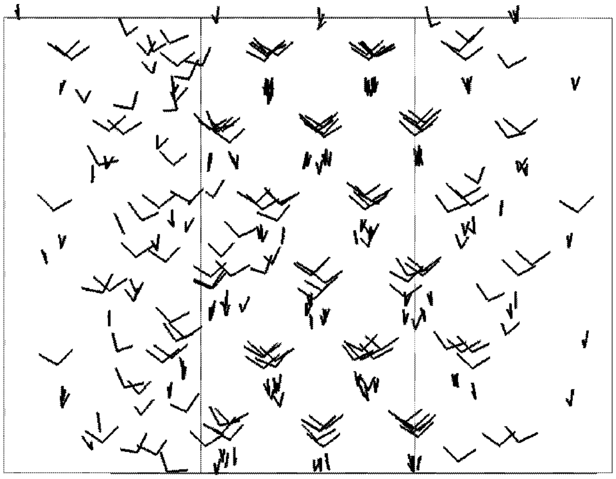

FIG. 4. Snapshot of the molecules viewed at the (110) plane after 200 ps of combined shearing and electrofreezing followed by electrofreezing alone for 400 ps, with an applied maximum shear rate of unity and electric field 0.5 V/Å. The direction of the homogeneous electric field (laboratory z axis) is vertical in the plot. ($\rho=0.92$ g/cm^3, $T=250$ K.)

The electrofreezing of water samples at ambient pressures yields cubic ice I crystals with few defects in a reasonable amount of simulation time (~ 200 ps). However, at temperatures below 250 K, and for densities below a certain threshold density (0.94 g/cm^3), simulations have failed to observe crystallization [5]. We performed exploratory simulations below these limits to see how our method performs in these cases. We report the results of two simulations: In the first case, $\rho=0.92$ g/cm^3 and $T_{sc}=250$ K, T_{sc} being the temperature to which the sample had been supercooled. A snapshot of the simulation cell viewed from the (110) direction can be seen in Fig. 4. The structure of the cubic ice can be clearly

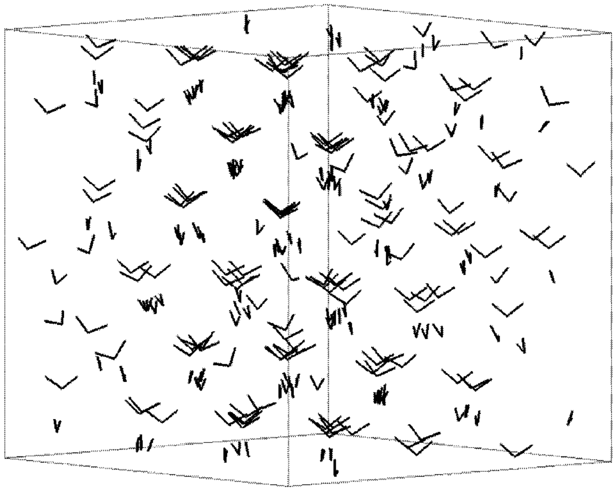

FIG. 5. Snapshot of the molecules viewed at the (110) plane after 1 ns of combined shearing and electrofreezing followed by electrofreezing alone for 500 ps, with an applied maximum shear rate of unity and electric field 0.5 V/Å. The direction of the homogeneous electric field (laboratory z axis) is vertical in the plot. ($\rho=0.95$ g/cm^3, $T=230$ K.)

identified because of the clearly visible hexagonal channels specific to this ice isomorph. In the second case (Fig. 5), the density was 0.95 g/cm^3 and $T_{sc}=230$ K. Again, the emerging cubic ice structure is evident.

The above results show that applied oscillatory shear was highly successful in concert with an applied electric field in breaking down the supercooled liquid's hydrogen-bonded network and rearranging the molecules so that the stable (polarized) crystalline phase is produced. In the light of these findings, the simple step of adding oscillatory shear (which comes at essentially no cost computationally) should be considered a very useful tool in the simulation of freezing, since it can result in an order of magnitude faster crystallization and, as in the lower density cases discussed above, bring the time for crystallization into a time frame reachable by simulation. It should be noted that the glassy (and thus nonergodic) nature of the supercooled initial samples can in itself result in substantial fluctuations in the crystallization speed, with the consequence that different starting configurations can yield different accelerations due to oscillatory shear. We are currently exploring this question.

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